CARBON DIOXIDE (CO_2) REFORMING OF METHANE TO SYNGAS OVER NI/SBA-15 CATALYST

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
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DECEMBER 2014

ABSTRACT

Global emissions of carbon dioxide (CO_2) was the main cause of human-induced global warming which is increased by 1.1% at 34.5 billion tonnes in 2012. There are many ways to reduce CO_2 product such as conversion of CO_2 to fuel, utilization of CO_2 as a chemicals feedstock and non-conversion use of CO_2 utilization of CO_2 for methane reforming to syngas will be studied over Ni/SBA-15. The SBA-15 and Ni/SBA-15 will be synthesized by conversional and impregnation method, respectively. The chemical and physical characteristics of the catalysts before and after catalytic test will be investigated using X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), Transmission Electron Microscope (TEM) and Brunauer–Emmett–Teller, Autosorb-1, Quantachrome (BET). SBA-15 have their unique structural features like high surface area, uniform and well defined pore topology. Nickel (Ni) based catalysts are one of the excellent catalyst systems for the CO_2 reforming to methane besides the noble metals catalysts. Ni/SBA-15 expected to exhibited excellent catalytic performance in terms of CO_2 conversion and long-term stability. The activity of the catalysts correlated strongly with the surface area and active site of the materials. This expectations was due to advantages of good structural stability and unique pore structural properties of SBA-15 as catalyst support and good active site of Ni, make this Ni/SBA-15 catalyst is suitable to be used for CO_2 reforming of methane. This expectation was due to the good structural stability and unique structural properties of SBA-15.

Keyword: *CO_2 reforming of methane, Synthesis gas, SBA-15, Ni/SBA-15, Hydrogen.*

ABSTRAK

Pelepasan secara besar-besaran gas karbon dioksida (CO_2) adalah punca utama pemanasan global. Hal ini disebabkan oleh populasi manusia yang meningkat sebanyak 1.1 % pada 34.5 bilion tan metrik untuk tahun 2012. Terdapat pelbagai kaedah untuk mengurangkan gas CO_2, antaranya adalah penukaran gas CO_2 kepada penjanaan, penggunaan gas CO_2 sebagai bahan mentah kimia dan penggunaan bukan-penukaran gas CO_2 dan pembaharuan gas CO2 untuk metana kepada syngas. Kaedah – kaedah ini akan dikaji melalui bahan Ni/SBA-15. SBA-15 dan Ni/SBA-15 yang akan disintesis menggunakan kaedah konversional dan impregnasi. Ciri-ciri kimia dan fizikal sebelum dan selepas ujian pemangkin akan disiasat menggunakan pembelauan sinar-X (XRD), Analisis Termogravimetri (TGA), Transmisi Elektron Mikroskop (TEM) dan Brunauer-Emmett-Teller, Autosorb-1, Quantachrome (BET). SBA-15 mempunyai ciri-ciri struktur yang unik seperti permukaan luas yang tinggi, seragam dan liang topologi yang baik. Nikel (Ni) yang berasaskan pemangkin adalah salah satu sistem pemangkin yang sangat baik untuk pembaharuan gas CO_2 kepada metana di samping pemangkin logam mulia. Ni/SBA-15 dijangka menunjukkan prestasi pemangkin yang sangat baik dari segi penukaran gas CO_2 dan kestabilan jangka panjang. Aktiviti pemangkin ini berkait rapat dengan kawasan permukaan dan permukaan yang aktif pada bahan tersebut. Jangkaan ini disebabkan oleh kelebihan kestabilan struktur yang baik dan sifat-sifat struktur liang yang unik pada SBA-15 sebagai pemangkin sokongan dan tapak aktif baik untuk Ni. Selain itu, Ni/SBA-15 juga menjadikan pemangkin ini sangat sesuai digunakan untuk pembaharuan gas CO_2 kepada metana disebabkan oleh kestabilan struktur yang baik dan sifat struktur yang unik SBA-15.

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LIST OF ABBREVIATIONS

X	Conversion
F_{in}	Flowrate in
F_{out}	Flowrate out
Y	Yield
C_i	Composition for each component
C_s	Composition for standard GC
A_i	Area for each component
A_s	Area for standard GC

1.0 INTRODUCTION

1.1 Background

The CO_2 reforming of methane got attention from environmental and industrial perspective because conversion of greenhouse gases into synthesis gas with a low H_2/CO ratio using nickel based catalyst. Nickel based catalyst is highly active for the CO_2 reforming of methane, but it is easily deactivated due to coke formation and metal sintering during the reaction (Jin-Kwon, et al., 2007).

Various materials such as metal oxides, mixed metal oxides, and zeolite have been examined as supports to develop nickel based catalyst resistant due to coke formation. The most supports that always used was metal oxide which is in fine powder due to its large surface area. However, using fine powder as support has disadvantage on this application because its particles tend to agglomerate into large particles at high temperature.

Nowadays, several researchers have shown that mesoporous SBA-15 compound can be used as catalyst support with high metal loading and dispersion without destroying the SBA-15 support pore hexagonal structure. SBA-15 compound are more favorable to be apply as catalyst support because of its mesopores sizes of 46-300 Å and high surface area of ~800 m^2/g. Moreover, the recent discovery of ordered large-pore mesoporous SBA-15 compound with three dimensional mesoporous networks has extended the applications in catalysis and separation because it has the advantage in the diffusion and transportation of large molecules compared to one-dimensional mesopore structures (Jin-Kwon, et al., 2007).

This paper reports to investigate Ni/SBA-15 as catalyst for the CO_2 reforming of methane to syngas. SBA-15 compound had been synthesis by conventional method and nickel particles were loaded into SBA-15 (Ni/SBA-15) using impregnation method. The catalytic results obtained in this study were compared with those between previous researches related to this study.

1.2 Motivation and problem statement

Carbon Dioxide (CO_2) is a major greenhouse gas that affected the atmosphere since 1896 which is enhanced to global warming. CO_2 in atmosphere can make a major effect of hurricanes (Knutson, et al., 1998), influence of El Nino phenomena (Feely, et al., 1999), reduce calcification of marines life (Barker & Elderfield, 2002; Riebesell, et al., 2000), and deglaciation (Montanez, et al., 2007). Therefore, the accumulation of CO_2 in atmosphere become a serious issues that need to be solved for environmental aspect.

The CO_2 emission involved fossil fuels when it burned from power plants comes from fuel combustion activities, industrial processes and natural gas processing, oil refineries, large industrial facilities and a few daily activities. The other types of CO_2 emitted from industrial production processes that can transform materials chemically, physically or biologically was uses of fuels as feedstocks in petrochemical processes (Chauvel & Lefebvre, 1989; Christensen & Primdahl, 1994).

From the Figure 1, CO_2 can be utilized in three major pathways which are as a storage medium for renewable energy, as a feedstock for various chemicals, and as a solvent or working fluid (Narasi & Davion, 2011). The uses of CO_2 to convert into various renewable fuels now widely supported by industry and governments because it can secure the future energy supplies and in order to decrease CO_2 emissions to atmosphere.

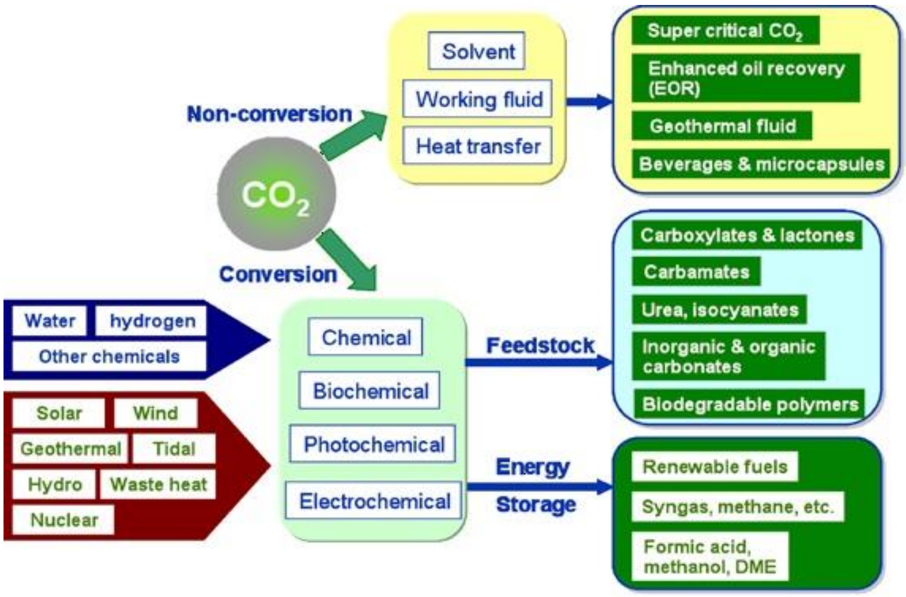

Figure 1.1: Different pathways for utilizing CO_2 (Narasi & Davion, 2011).

CO_2 can also be utilized as a part of different processes without convert it into other chemical structures. The injection of supercritical CO_2 into exhausted oil wells to improve the further recovery of oil is entrenched. In fact, this is in no time the main monetarily practical innovation for carbon capture and storage (CCS). It has been evaluated that CO_2 injection can build oil recovery from a well-draining by around 10 to 20 % of the first oil set up. Additionally, CO_2 can be utilized to recover methane from unmined coal creases. It has been estimated that in the U.S. alone, 89 billion barrels of oil could be recovered using CO_2, prompting a stockpiling of 16 Gt of CO_2 in the drained oil reservoirs (Shailesh, et al., 2013).

In addition, to produce biomass, chemical and electrochemical processes have been converted from CO_2 to other energy storage chemicals such as syngas, formic acid, methane, ethylene, methanol, and dimethyl ether (Olah, et al., 2009). Although it is more productive to utilize the electrical energy derived from renewable power sources straightforwardly, their variability represents an issue for many industries. Besides, the circulation base for hydrocarbon fuel is settled. At last, chemicals, for example, formic acid may be a valuable storage medium for H_2 that could be utilized as a part of energy components or blazed specifically (Narasi & Davion, 2011).

The hydrogen (H_2) market offers an energy for the future world that claimed as clean, safe and multifunction fuel. Production of H_2 can be produced from a chemical processes through a fossil fuel, biomass conversion, electrolytic, biophotolololytic, or thermochemical splitting of water. H_2 can stores chemically or physically and converts to electrical and heat energy for the other uses. The biological world began developing H_2 market three billion years ago using H_2, C, and O_2 to reduce the cycle of photosynthesis and respiration in order to secure the earth. The human-engineered H_2 economy can take similar advantages of H_2 from chemical and physical interactions with materials to adaptably link and variety of energy sources for multitude of energy uses (Butterfield, 2013).

In U.S., hydrogen is right now created 0.09 Mtons/yr on a production through steam reforming of natural gas. These days, the majority of the hydrogen originate from fossil fuels is utilized as a part of the manure, petroleum, and compound commercial enterprises. Common gas assets will be sufficient for a few decades to extend this ability to backing the Freedom CAR and Fuel Initiative. By 2030, it is expected that the utilization of hydrogen in fuel cell controlled vehicles and light trucks could supplant production of 18.3 MB everyday of petroleum. Accepting that hydrogen controlled vehicles have 2.5 times the energy efficiency of enhanced fuel vehicles, this diminishment in petroleum utilization would require the annual production of pretty nearly 0.55 Mtons of hydrogen by 2030. On the off chance that the majority of this hydrogen were delivered by petroleum changing, the net funds in petroleum utilization would be 11 MB every day. The aggregate energy used for transportation, incorporates a significant segment of different sorts of vehicles that need represents a more challenging test to hydrogen generation (Butterfield, 2013).

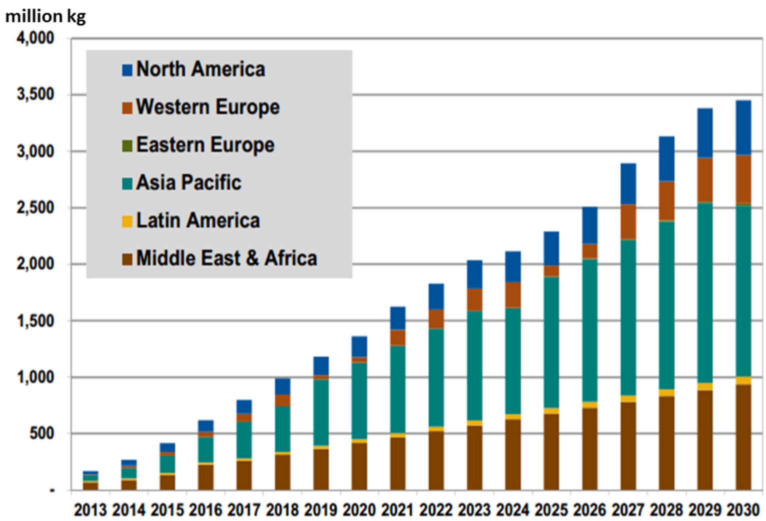

Figure 1.2: Hydrogen consumption by region of production (Butterfield, 2013)

There are many ways to reduce CO_2 and make it to useful product such as conversion of CO_2 to fuel using biomass, utilization of CO_2 as a chemicals feedstock, non-conversion use of CO_2 and also CO_2 reforming to syngas (Narasi & Davion, 2011). CO_2 reforming of methane, also known as dry reforming ($CH_{4(g)} + CO_{2(g)} \leftrightarrow 2CO_{(g)} + 2H_{2(g)}$) to syngas, which is can be used in various downstream chemical processes such as methanol production, Fischer-Tropsch synthesis processes and in carbonylation, hydrogenation, and hydroformylation processes (Amin, et al., 2012). In this work, CO_2 reforming of methane will be studied over Ni supported on mesoporous SBA-15 (Ni/SBA-15). This catalyst will be synthesized by conventional and impregnation method, respectively.

Due to previous research, SiO_2 and γ-Al_2O_3 have been the most often used for dry reforming of methane. Noble metal-supported catalysts (Rh, Ru, Pd, Pt, Ir) were founded to have promising catalytic performance in terms of conversion and selectivity for reforming of methane. But, because high cost of its make them not suitable choice for this process (Bradford

& Vannice, 1996; Fan, et al., 2009). Ni based catalyst is one of a good replacement for noble metals to be supported on SBA-15 because of higher activity, lower coke formation, and higher stability than Ni based catalysts supported on SiO_2 or γ -Al_2O_3 for the CO_2 reforming of methane (Jin-Kwon, et al., 2007).

1.3 Objective of Study

The objective of this study are to synthesis Ni/SBA-15 catalyst with suitable properties for CO_2 reforming of methane to syngas with high conversion and yield.

1.4 Scopes of Research

The scopes of this research are to mainly study about:

- To synthesis Ni/SBA-15 by using impregnation method with weight percentage of Ni loading (1, 3, 5 wt %).
- To characterize the catalyst properties by using X-ray diffraction (XRD), Thermogravimetric Analysis (TGA), Transmission Electron Microscope (TEM) and Brunauer–Emmett–Teller, Autosorb-1, Quantachrome (BET).
- To test catalyst performance via CO_2 reforming of methane to syngas.

1.5 Main Contribution of This Work

The following is the contribution:

- Prior to our supervisor’s guidance in helping us learn and venture into Ni/SBA-15 on CO_2 reforming of methane to syngas.
- Be able to study the effects of weight percentage of Ni loading, characterization of catalyst and catalytic testing in CO_2 reforming of methane to syngas using fixed-bed reactor.

1.6 Organisation of This Thesis

The structure of the thesis is outlined as follow:

Chapter 1 described about the relationship between greenhouse gases that affected earth and CO_2 reforming of methane to syngas. Since H_2 can produce a lot of useful product that can reduce greenhouse gases produce in our daily life, it give a motivation to do a research about CO_2 reforming of methane to syngas using Ni/SBA-15. In this chapter also include scope, hypothesis and main contribution of this research.

Chapter 2 provides an overview of CO_2 reforming of methane using Ni/SBA-15 and Ni/SBA-15 synthesis by impregnation method. This chapter also provides a brief review on previous study on greenhouse gas emission, the best support material on SBA-15. A comparison that directly affect the performance between previous research and this research.

Chapter 3 described about the methodology involved in this research. The synthesis of SBA-15 and Ni/SBA-15 using conventional and impregnation method respectively, characterization of catalyst and catalytic activity testing for CO_2 reforming of methane.

Chapter 4 discussed on the effect of Ni loading with 1 wt%, 3 wt%, and 5 wt% on SBA-15 for CO_2 reforming of methane. The discussion on the reaction performance was related to the catalyst properties that obtained from XRD, BET, TGA, and TEM.

Chapter 5 draws together a summary of the thesis and outlines for the future work which might be derived from the experiment developed in this work.

2.0 LITERATURE REVIEW

2.1 Greenhouse Gas Emission

Svante Arrhenius (1859-1927) was a Swedish scientist that claim in 1896 that fossil fuel combustion may eventually result in enhanced global warming. He proposed a relation between atmospheric CO_2 concentrations and temperature. In the late 1950's and early 1960's, Charles Keeling used the newest technologies available to produce atmospheric CO_2 concentration curves in Antarctica and Mauna Loa. Therefore, fear began to develop that a new ice age might be near. The media and many scientists ignored scientific data of the 1950's and 1960's in favor of global cooling (Maslin, 2004; Enzler, 2014).

In 1940, there were advancements in infrared spectroscopy for measuring long-wave radiation. Around then it was demonstrated that increasing the amount of atmospheric carbon dioxide resulted in more absorption of infrared radiation. It was also discovered that water vapor consumed entirely unexpected sorts of radiation than CO_2. Gilbert Plass summarized these results in 1955. He concluded that adding more CO_2 to the air would catch infrared radiation that is generally lost to space, warming the earth.

Finally, in the 1980's, the global annual mean temperature curve started to rise. In the late 1980's, the curve began to increase so steeply that the global warming theory began a hot news topic that was repeated on a global scale. A complete media circus evolved that convinced many people we are on the edge of a significant climate change that has many negative impacts on our world today. Stephen Schneider was an experts about world's leading global warming that had a first predicted of global warming in 1976 (Maslin, 2004; Enzler, 2014).

In the 1990's scientists started to question the greenhouse effect theory, because of major uncertainties in the data sets and model outcomes. In 1998, it was globally the warmest year on record, followed by 2001, 2002, 2003 and 1997. The 10 warmest years on record have all occurred since 1990. So far not many measures have been taken to do something about climate change. This is largely caused by the major uncertainties still in the theory. Therefore in 1998 the Kyoto Protocol was negotiated in Kyoto, Japan and it requires participating countries to reduce their anthropogenic greenhouse gas emissions (CO_2, CH_4, N_2O, HFCs, PFCs, and SF_6) by at least 5% below 1990 levels in the commitment period 2008 to 2012 (Maslin, 2004; Enzler, 2014).

Environmental change made by anthropogenic greenhouse gases has created the most basic biological issues standing up to the all-inclusive gathering. The supporters of the Protocol applauded it as a jump forward in overall air approach, in light of the fact that it secured an extensive worldwide framework for extending and creating climate security practices later on. Foes to the Protocol rejected it as a "significantly blemished comprehension that makes sense of how to be both fiscally inefficient and politically strange" (McKibbin & Wilcoxen, 2002).

Actually, after years of dull transactions on its solid execution, the Protocol has yet to go into energy, sitting tight for Russia to interpret its certain open reports into lawful sanction. Additionally, the U.S. refusal to approve the Protocol and the full tradability of discharge privileges surrendered to the previous Eastern Bloc in overabundance of its foreseen future the same old thing discharges (supposed hot air) infer that the present round of the Kyoto Protocol is liable to fulfill almost no regarding worldwide emanation decreases (Buchner, et al., 2002). This development appears to affirm the position of the Protocol's adversaries that its key methodology – setting targets and timetables for discharge decreases - is truly imperfect. Against this foundation, I need to give a discriminating evaluation of the Protocol's expected execution and examine potential changes to encourage adequacy and productivity in ensuing duty period (Böhringer, 2002).

2.2 CO_2 Reforming Of Methane

As the way to reduce CO_2 gas that affect the atmosphere, previous researchers have done invention such as in food industry they use it in food processing, preservation, food packaging, beverage carbonation, coffee decaffeination, and wine making. In other industry, CO_2 was used it to enhance oil recovery, urea fertiliser production, water treatment, steel manufacture, metal working, pulp and paper processing, and many of it that used in our life. Furthermore, CO_2 was used to make the medicine in pharmaceutical sector. From the further research, CO_2 can convert to various useful things such as liquid fuel, electricity and synthesis gas (syngas) as shown in Figure 3 (Brinckerhoff, 2011).

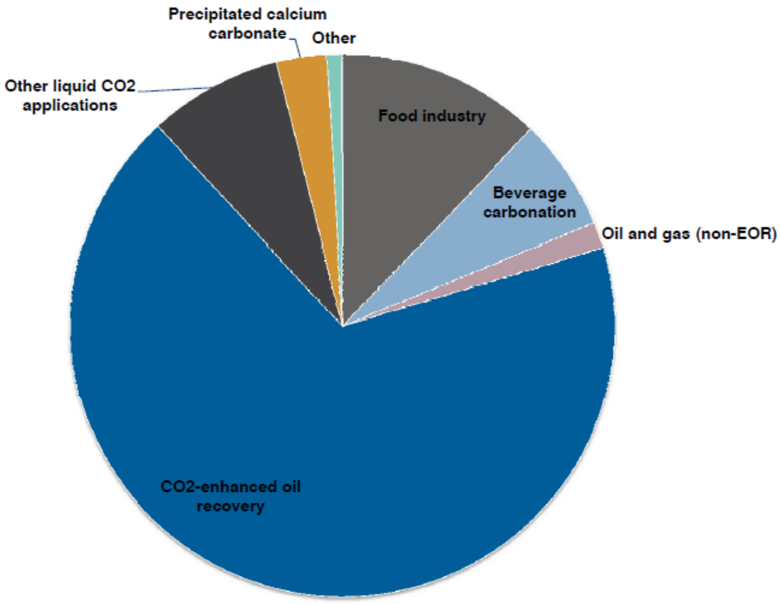

Figure 2.1: Existing bulk Carbon Dioxide (CO_2) market (Brinckerhoff, 2011)

2.21 Syngas

Synthesis gas or syngas can be produced from different materials that contain carbon. These can include in biomass, plastics, coal, municipal waste or similar materials. Syngas can produced from gasification or pyrolysis of carbonaceous materials. Gasification can be involved these subjecting materials to high temperatures, in controlled presence of oxygen with limited combustion to provide thermal energy to sustain the reaction. Man-made vessels, or alternatively could be conducted in-situ can be occurred in the gas of underground coal gasification. There are two types of gasifier. One of it is fuel to the gasifier where it is a recent biological origin, such as wood or organic waste, the gas produced by the gasifier is considered to be renewable and that is the power produced by the combustion. Second is fuel to the gasifier where it is a waste stream, the conversion to power in this manner has the combined benefit of the conversion of this waste into useful products. Generation of renewable power, conversion of problematic wastes to useful fuels, economical onsite power production and reduced transmission losses and reduction in carbon emissions are the benefits of synthesis gas. From the Figure 4, there are many useful product can produce from syngas and also can reduce the emission that affected the atmosphere (Bhd., n.d.)

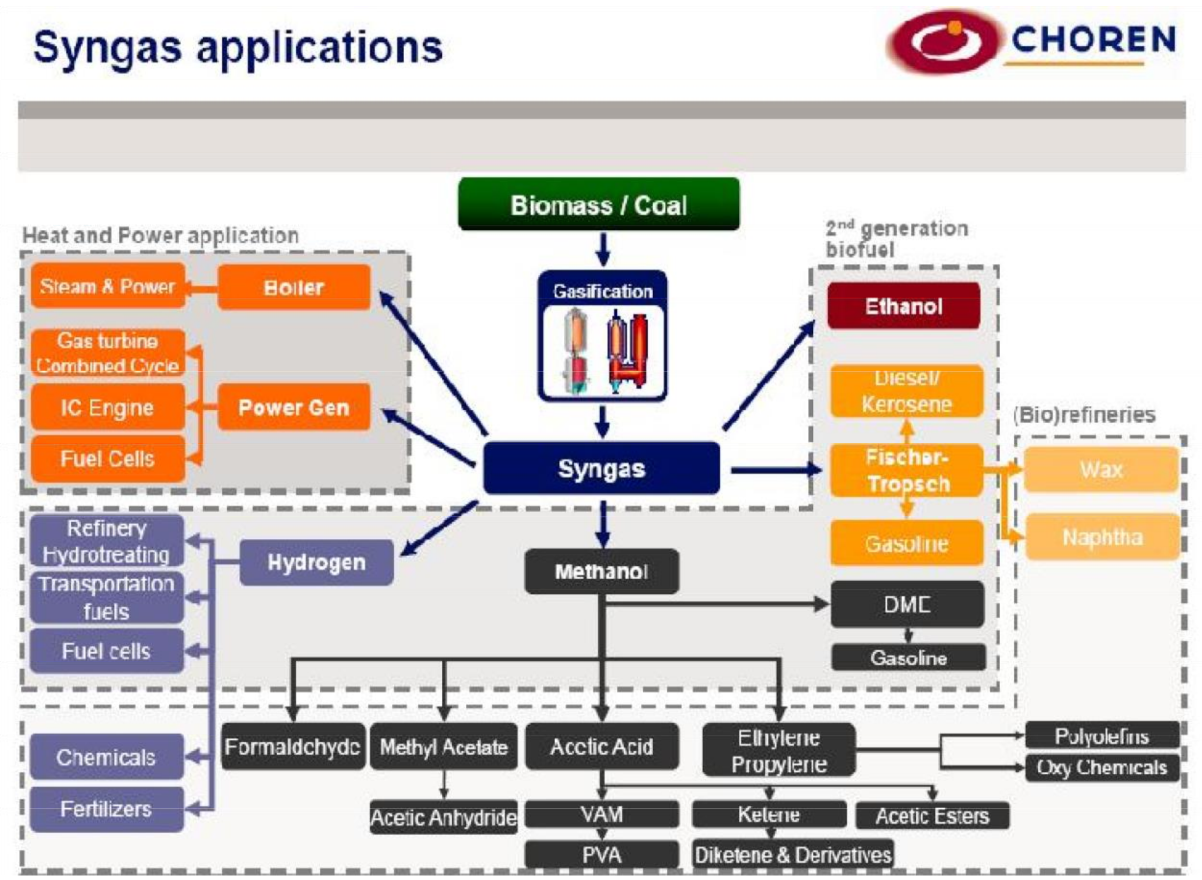

Figure 2.2: Applications of syngas from Biomass/coal

These last issues have animated examination into the development of synthesis gas by the carbon dioxide reforming of methane (dry reforming). The carbon dioxide reforming of methane, indeed, has been of enthusiasm for quite a while, going back to as right on time as the 1920's (Fischer & Tropsch, 1928), however it is just as of late that enthusiasm for it has quickly expanded for both ecological and business reasons. This reaction can performed as:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (1)$$

This procedure has numerous attractive preferences over dry reforming: (i) Synthesis gas has a CO/CO_2 ratio without further, post-reformer reaction. (ii) The utilization of CO_2 implies that it is an appealing course toward CO_2 relief in stationary anthropogenic sources. (iii) It permits the conversion of methane, beforehand a waste part of oil stores, into a financially alluring feedstock (Zhang, et al., 2003).

2.22 Hydrogen (H_2)

Other settled carbon stores, for example, coal or biomass feedstocks, could be utilized to create hydrogen through reforming methods. With respect to natural gas, these assets create more or less twice as much CO_2 every amount of hydrogen produced. This element puts extra weight on the advancement and economics of carbon sequestration. These feedstocks additionally contain variable measures of water, sulfur, nitrogen, and nonvolatile minerals that considerably convolute reforming process engineering. By and by, if a monetary and safe system for CO_2 sequestration is created, financial elements (the general accessibility and generally minimal effort of coal) may empower coal to play a noteworthy mid-term part in hydrogen era. Dependence on coal as a sole wellspring of vitality for producing hydrogen for Freedom CAR transportation needs would oblige multiplying of current local coal generation and utilization. Two effective methods for hydrogen production from coal or biomass are being worked on: (i) reforming under partial oxidation and (ii) a joined cycle strategy that uses $Ca(OH)_2$ to constrain the reforming reaction by adsorbing CO_2 as it is produced (Lin, et al., 2002).

In spite of the fact that the innovation is accessible for creating hydrogen in amount through reforming of natural gas or potentially other carbon holds, the hydrogen produced is not of sufficient purity for immediate use in the low-temperature (<130°C) fuel cells being worked on for transportation applications. The last stage in current reforming processes, the water-gas shift reaction, leaves enough carbon monoxide (CO) in the product stream to toxin the fuel cell anode. Current strategies for evacuating this leftover CO incorporate pressure-swing adsorption, particular oxidation, or catalytic methanation, all of which add expense and multifaceted nature to the fuel handling framework. Essential examination can supply elective answers for this issue, which could come as more active catalysts for the low-temperature water-gas shift reaction, better gas stream separation processes and membranes, or CO-tolerant catalysts at the fuel cell anode (Lin, et al., 2002).

2.23 Methane

Since methane was discovered to be a dominating segment of regular gas, late studies on the usage of natural gas have been focused only on catalytic conversion of methane to syngas. As characteristic gas is found in numerous areas around the globe, the catalytic conversion of methane would create syngas which is a crude material for some mechanical items, for example, manures, explosives, chloroform and carbon tetrachloride. Syngas is additionally a vital source of methanol. The procedure of POM (partial oxidation of methane) shows gentle exothermicity. Contrasted with steam reforming, the catalytic partial oxidation is assessed to offer vitality cost decrease of around 30% since the response is exothermic. An included favorable position is that the syngas created has the CO/CO_2 molar ratio of around 2 and this makes the POM process perfect for the creation of amalgamation gas for utilization in methanol or Fischer-Tropsch synthesis (Habimana, et al., 2009).

2.3 Support Material

2.31 Silicon Dioxide (SiO_2) and Aluminium Oxide (Al_2O_3)

A few decade ago, the research on CO_2 reforming of methane has been developed of improved materials using catalytic reaction. Different types of catalysts have been used for dry reforming but from an industrial perspective, Ni based catalysts was the most often catalysts for dry reforming of methane. This reactions are considered the most promising which is exhibit high catalytic activity (Ferreira-Aparicio, et al., 1998), are readily available, and cost effective.

Since 1979 (Sodesawa, et al., 1979) and 1980 (Chubb, 1980), Ni/SiO_2 and Ni/Al_2O_3 have been the most often used catalysts for dry reforming of methane. This interest has been mostly due to SiO_2 and γ-Al_2O_3 with melting points of 1973°C and 2318°C (Richardson, 1989) having high mechanical strength and relatively low cost. Although noble metal-supported catalysts (Co, Ni, Ru, Rh, Pd and Pt. La and Zr) were founded to have promising catalytic performance in terms of conversion and selectivity for reforming of methane, the high cost of noble metals makes them a less than ideal choice (Bradford & Vannice, 1999; Fan, et al., 2009).

2.32 Metal Oxide

Most normal metal oxide for methane reforming, for example, α- and γ-Al_2O_3, MgO, $MgAl_2O_4$, SiO_2, ZrO_2, TiO_2, CeO_2, La_2O_3, and CaO have been utilized as support materials. These supports have great porosity, which permits bigger surface region. Support assumes an urgent part since it focus the last molecule size of the metal, with its pore structure, morphology, and stage moves that it can experience. Moreover, a support can have a chemical part too, by initiating one or more reaction steps (Liu, 2006).

Wang et al. demonstrated that solid interaction in the middle of metal and support would make a catalyst more impervious to sintering and coking, which would make a more steady catalyst (Wang & Lu, 1998).

Bradford et al. found that Ni-Ni bonds for Ni/MgO catalysts can be settled by NiO-MgO strong arrangement. Furthermore it can anticipate carbon dispersion into nickel particles. Likewise, they saw that the support impacts the catalyst action by changing the electron donating capacity of the lessened nickel surfaces. With the Ni/TiO_2 study, they found that an in number metal-support interaction happens, which would bring about blockage of the active nickel sites. These blockages are because of the relocation of TiO_x-species from the TiO_2-bearer (Bradford & Vannice, 1996).

These couple of illustrations demonstrate the impact of the support on catalysts. Nonetheless, a support can likewise partake in catalytic reaction. Supports with an essential nature, for example, MgO, are known not the activation of steam, and separation of steam into OH and H species. Carbon stores can prompt active site blocking and influence the catalyst reactivity and stability. The support can likewise assume a part in smothering carbon deposition. ZrO_2 and CeO_2 have been known able to oxidize stored carbon. Further, they are equipped for taking part in the catalytic reaction by oxidizing or diminishing reaction intermediates. Dong et al. considered methane reforming over $Ni/Ce_{0.15}Zr_{0.85}O_2$ catalysts. They concluded that there were two sorts of active sites that exist, one for methane activation and one for steam or oxygen activation. Ceria, can store, discharge, and exchange oxygen species, which brings about an upgraded capacity to avoid carbon formation (Dong, et al., 2002).

2.33 Nickel (Ni)

Among the catalysts examined, Ni is one of a good replacement for noble metals, due to its comparable catalytic performance and low cost in terms of methane conversion and selectivity to synthesis gas. However, Ni based catalysts are more easily deactivated, because of carbon deposition and active metal species sintering and carbon deposition cannot be avoided over nickel-supported catalysts and for a CO/CO_2 molar ratio of unity (Kroll, et al., 1996; Rostrup-Nielsen & Hansen, 1993).

From the past theory and experimental studies, it was affirmed that amount of Ni particles have a superior capacity to smother the carbon deposition (Xu, et al., 2011). By and by, binding the size of Ni particle inside of the nanoscale measurement is troublesome, on the grounds that the sintering of the Ni particles effectively happens under the serious reaction states of dry reforming of methane. As of late, it was accounted for that the tying down impact, an idea that was depicted by Yermakov, can encourage the arrangement of the active Ni nano-clusters with high dispertion under the reaction condition (Cai, et al., 2014).

For the most part, the catalyst utilized for the dry reforming of methane are arranged into two gatherings: (i) supported noble metals (Pt, Pd, Rh, Ru) and (ii) non-noble transition metals (Ni, Co, Fe). In examination to noble and other transition metals, Ni is by all accounts the most encouraging decision on the grounds that it is less expensive, and relatively more active and selective. However Ni based catalysts tend to deactivate because of sintering, coking, phase change and loss of active segment (Fan, et al., 2009).

Carbon decomposition has long been perceived as the principle explanation behind metal supported catalysts deactivation in methane reforming reaction. Various theory and experimental studies on dry reforming of methane instrument have uncovered that when dry reforming of methane procedure, methane is decayed first on active metal locales to frame responsive surface carbonaceous species close gas-metal interface, which are then oxidized to CO by collaborating with oxygen that started from CO_2 (Huirache-Acuña, et al., 2013). In perspective of that, the rate of coke deposition on catalyst surface is reliant on the relative rates of the carbon formation and its oxidative removal. Thus, if the rate of the carbon gasification by CO_2 is not exactly the rate of carbon formation, the huge volume of carbon deposit will amass over gas-metal interface, which can thereafter polymerize. These polymerized carbon particles can add to catalysts deactivation through two ways: (i) embodying the active metal particles or diffusing through the active metal subsequent to dissolving, and (ii) isolating active metal particles from the support (Cai, et al., 2014). It is accepted that the carbon formation is more effortlessly supported by acidic supports than essential support and also, coke deposition happens more effectively on greater particles than littler ones.

Since Ni molecule size and its dispersion over support has an in number impact on catalyst deactivation and carbon deposition. CO beat chemisorption analyses were done to watch the progressions in Ni molecule size and their circulation. The most noteworthy active metal dispersion and littlest metallic crystallite size were achieved for Ni, which were in charge of its better strength and resistance towards coking. While among all the tried catalysts most reduced Ni dispersion and greatest Ni crystal size were seen in the event of Ni-Ce catalyst. Actually the most noteworthy coke deposition if there should arise an occurrence of Ni-Ce catalyst is because of the vicinity of greater Ni molecule in this catalyst (Cai, et al., 2014).

2.4 Santa Barbara Amorphous 15 (SBA-15)

Santa Barbara Amorphous 15 silica (SBA-15) shows fascinating textural properties, for example, huge particular surface areas (over 1000 $m^2 \cdot g^{-1}$), uniform-sized pores (in range 4–30 nm), thick system walls, little crystallite size of essential particles and reciprocal textural porosity. The upsides of SBA-15 material as support incorporates likewise its high surface-to-volume ratio, variable structure creations and high thermal stability (Huirache-Acuña, et al., 2013). Mesoporous silicas, for example, SBA-15 have an alternate pore structure from mesoporous aluminas. Mesoporous silicas show common sort IV isotherms and steep hysteresis circles (sort H1) at high relative weight, demonstrating a huge and tube shaped pore structure (Kima, et al., 2007).

Figures 5(a) and 5(b) shows two high determination transmission electron microscopy (HRTEM) micrographs of research center synthetized SBA-15 mesoporous silica calcined at 550°C. The SBA-15 shows hexagonal pores in a 2D exhibit with long 1D channels (p6mm plane gathering) (Zhang, et al., 2005). The channels are interconnected by little micropores. Subsequently, SBA-15 displays essentially mesoporous structure and has a little amount of micropores. The huge pore size of this mesoporous material can alleviate the dispersion boundary for the reactants and the items. On the other hand, pure siliceous SBA-15 has an electronically unbiased structure and needs Brønsted corrosiveness. This issue could be evaded by SBA-15 alteration with a specific end goal to make this mesoporous substrate more adaptable as far as its conceivable applications, either as a basic material or support, in adsorption processes, separation, catalysis or as evaluated for this situation, as support of catalysts utilized as a part of hydrodesulfurization (HDS) reactions in petroleum refining procedures (Huirache-Acuña, et al., 2013).

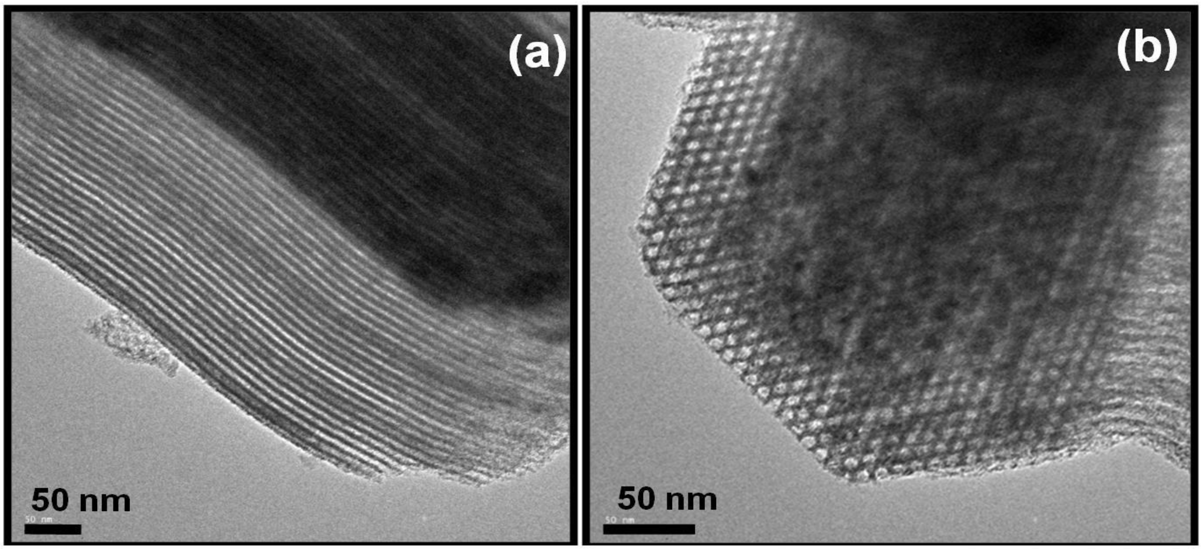

Figure 2.3: High resolution transmission electron microscopy (HRTEM) micrographs of SBA-15 mesoporous silica. The size and morphology of the highly ordered hexagonal pores in a 2D array (a) with long 1D channels (b) (p6mm plane group) can be observed.

There are numerous ways to deal with plan better SBA-15-supported catalysts, for example, replace the support properties by substitution of Si^{4+} by distinctive cations, functionalization with diverse groups, and so forth, changing the active stage part, differing the preparation system, and so on. By and large, the studies in this field plan to get connections between distinctive physical and substance properties of the support and active stages and catalyst execution for hydrotreating reactions, for example, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and/or hydrodearomatization (HDA). Late correction by Rahmat et al. on the SBA-15-based catalysts centered with respect to the application in biorefinery generation (Rahmat, et al., 2010).

While trying to grow new more compelling mesoporous silica support, the (HDS) action of SBA-15-supported catalysts were contrasted and those supported on hexagonal mesoporous silica (HMS) and SBA-15 demonstrating diverse morphology and pore diameter. The SBA-15 has altogether bigger pore diameter than those of HMS and SBA-16, and both SBA-15 and SBA-16 substrates are steadier than HMS, because of their thicker pore dividers (Huirache-Acuña, et al., 2013). Interestingly, it was found that the catalytic reaction of HMS- and SBA-15-supported catalysts in the HDS reaction of DBT was comparative. This was a shocking result, in light of the fact that, in correlation with the HMS, the SBA-15 demonstrated a bigger pore diameter. The comparable HDS activity of both HMS- and SBA-15-based catalysts may demonstrate that the wormhole mesostructure of HMS offers comparative